PATENT SPECIFICATION

761,307

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COMPLETE SPECIFICATION

Dielectrics

We, ERIE RESISTOR CORPORATION, a corporation of the State of Pennsylvania, United States of America, located at 644, West Twelfth Street, Erie, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is intended to improve the life and dielectric losses of high dielectric constant barium titanate ceramics by the addition of a small fraction of a percent of Cr_2O_3. The Cr_2O_3 additions are particularly effective at high temperatures. The effect of the Cr_2O_3 additions apparently is to stabilize the ceramic preventing the changes which increase the losses and decrease the life. The Cr_2O_3 additions do not change the dielectric strength, the aging, the voltage coefficient of capacity, or other characteristics and apparently act independently of other additions which modify the properties in other respects.

It has been proposed in Patent Specification No. 574,577 to provide a ceramic composition having a high permittivity and formed by firing a ceramic mix comprising barium titanate and if desired up to 10% but usually not more than between 1% and 2% of chromium oxide.

This invention consists in a high dielectric constant barium titanate ceramic dielectric having at least 70% by weight $BaTiO_3$ and .1 to less than .5% by weight Cr_2O_3.

In the accompanying drawing, Figure 1 is a curve of dielectric constant and losses against Cr_2O_3 additions; Figure 2 is a life curve; and Figure 3 is a curve of losses and insulation resistance against time.

Barium titanate ceramic dielectrics containing from 70 to 100% barium titanate and having dielectric constants of from 600 to 6,000 or more are widely used in ceramic capacitors. One of the properties of such dielectrics is that the life at high operating temperatures tends to be low and the losses increase substantially with time. Since high operating temperatures (85° C.—125° C.) are becoming more common, it is desirable that the life of the barium titanate ceramic dielectrics be improved. Since the high temperatures also increase the dielectric losses, it is further desirable that the increase in dielectric losses with time be eliminated. It has been discovered that both of these objects can be achieved by additions of the order of .2% of chromium oxide (Cr_2O_3). The effect of the chromium oxide additions apparently is to prevent the migration of the oxygen in the ceramic crystal lattice and to stabilize the dielectric properties preventing the deterioration of the dielectric strength with time which leads to failure of the dielectric and likewise preventing the increase in dielectric loss which has heretofore taken place particularly at the normal operating temperature (85° C.) and most noticeably in higher operating temperatures up to 125° C. While chromium oxide additions have been proposed for barium titanate ceramics, the chromium oxide additions have been in relatively large amounts so as to alter the characteristics of the barium titanate and make it more like a resistor than a dielectric. It has not heretofore been appreciated that minute or almost trace additions of chromium oxide in the range of a small fraction of 1% would materially retard the deterioration of the dielectric properties of barium titanate ceramics with time so that the useful life would be greatly increased.

The effect of the chromium oxide additions is independent of other additions made to the barium titanate ceramic for the purpose of making other alterations in the dielectric properties. The chromium oxide additions do not increase the dielectric strength, but apparently only prevent the deterioration of the dielectric strength with time under high temperature conditions and likewise prevent a corresponding increase in the dielectric losses. The effect of the chromium oxide additions is apparently limited to barium titanate ceramics containing 70 or more percent by weight of barium titanate. Addition of chromium oxide

[~~Price 3s. 6d.~~]

to TiO_2 does not produce a significant variation in either the life or dielectric losses.

The dielectric properties of barium titanate ceramics containing 70 or more percent barium titanate vary in dielectric constant from 600 to 6000 or more depending upon the specific composition. This range has been investigated and all the barium titanate mixes have their life improved by the small fraction of 1% chromium oxide additions. Representative formulations coming within this range of dielectric constant are as follows:

K1200
- 88 $BaTiO_3$
- 10 $SrZrO_3$
- 2 (CaF_2, $CaCO_3$, Fe_2O_3)

K2000
- 90 $BaTiO_3$
- 10 $SrTiO_3$

K3500
- 88 $BaTiO_3$
- 10 $SrZrO_3$
- 2 Flux e.g. Magnesium Silicate

K6000
- 80 $BaTiO_3$
- 10 $SrTiO_3$
- 10 $CaZrO_3$

In the above formulations, the number following the "K" is the typical dielectric constant, which is subject to variations resulting from the manufacturing processing. In all these formulations, the percentages are in parts by weight. Throughout the range or formulations from dielectric constants of 600 to 6000 or more and percentages of barium titanate ranging from 70 to 100, the small fraction of 1% chromium oxide additions have the same kind of effect, namely, increase of life particularly at the higher operating temperatures and preventing the increase in dielectric losses with time. The additions of chromium oxide may be as little as .1 of 1% and as much as ⅓ of 1% with the optimum characteristics obtained at from 1/5 to ¼ of 1%. At additions of ½ of 1%, the dielectric constant is depressed and the dielectric losses are increased. With additions of more than ½ of 1% chromium oxide, the dielectric begins to take on properties of a resistor rather than a dielectric.

Figs. 1, 2, and 3 show the properties of the K3500 mix with additions of chromium oxide. Fig. 1 shows the effect of various percentages of chromium oxide additions on the power factor and dielectric constant of the K3500 mix. Curve 1 shows that as chromium oxide is added to the K3500 mix, the dielectric constant increases reaching a maximum at about .1 of 1% and then continually decreases as the percentage of chromium oxide is increased. The power factor or dielectric losses increase until [illegible] of 1% chromium oxide addition is made and thereafter decreases until the chromium oxide reaches ⅓ of 1% after which the losses begin to increase. It is therefore desired to use chromium oxide in an amount of substantially ¼ of 1%, but in any event at least 0.1% and less than ½ of 1%. On the basis of overall performance, balancing the dielectric constant against the losses, ¼ of 1% chromium oxide is at the middle of the optimum range which extends from .2 to .3 of 1% chromium oxide.

Fig. 2 shows the relative life at 125° C. under a direct current voltage of 100 volts per mil of the standard K3500 mix without any chromium oxide additions and for the K3500 mix with the indicated percentages of chromium oxide additions. As can be seen from Fig. 2, the K3500 mix with the chromium oxide additions has well over 10 and in many cases 100 times the life of the standard K3500 mix without the chromium oxide additions. The difference in life under voltage stress is greater at higher temperatures. This is important, because the life under voltage stress is in general adequate at the lower temperatures.

In Fig. 3, which is a plot of the power factor of losses against time, it can be seen that while the standard K3500 mix increases in losses from 1 to 6% in 500 hours, the addition of the order of .2% chromium oxide entirely eliminates the increase in losses. Not only does the small amount of chromium oxide reduce or eliminate the increase in losses, but it also prevents a falling off in insulation resistance.

While the results shown in Figs. 1—3 are for the K3500 mix, the same kind of results are obtained with other formulations running from K600—6000 or more and containing 70 or more percent barium titanate by weight. In all these formulations, the chromium oxide additions should be kept to less than ½ of 1% and the optimum characteristic will be obtained in the region of .2 of 1%. In fact, the phrase "substantially .2 of 1%" is perhaps the most satisfactory designation for the amount of chromium oxide additions in which the optimum described effects are obtained.

What we claim is:—

1. A high dielectric constant barium titanate ceramic dielectric having at least 70% by weight $BaTiO_3$ and from 0.1 to less than 0.5% by weight Cr_2O_3.

2. A high dielectric constant barium titanate ceramic dielectric having at least 70% by weight $BaTiO_3$ and of substantially .2% by weight Cr_2O_3.

3. The ceramic of Claim 1 containing in addition a minor percentage of $SrZrO_3$.

4. The ceramic of Claim 1 containing in addition a minor percentage of $SrTiO_3$.

5. The ceramic of Claim 1 containing in addition a minor percentage of $SrTiO_3$ and $CaZrO_3$.

MARKS & CLERK.

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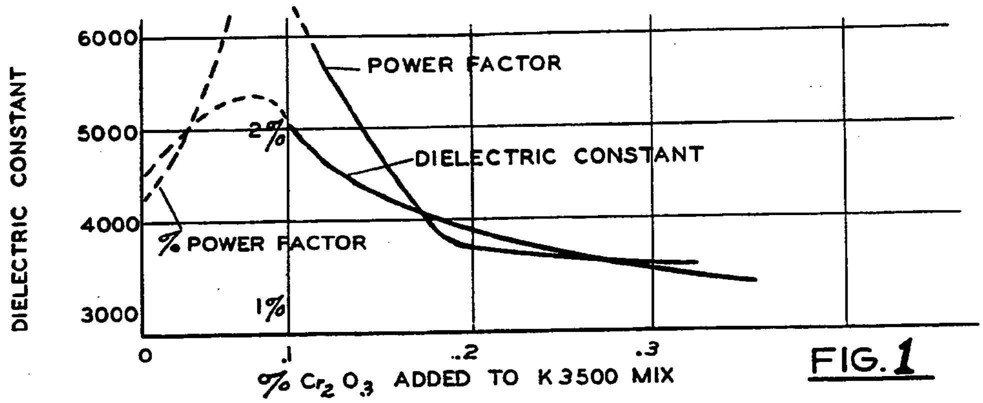

FIG. 1

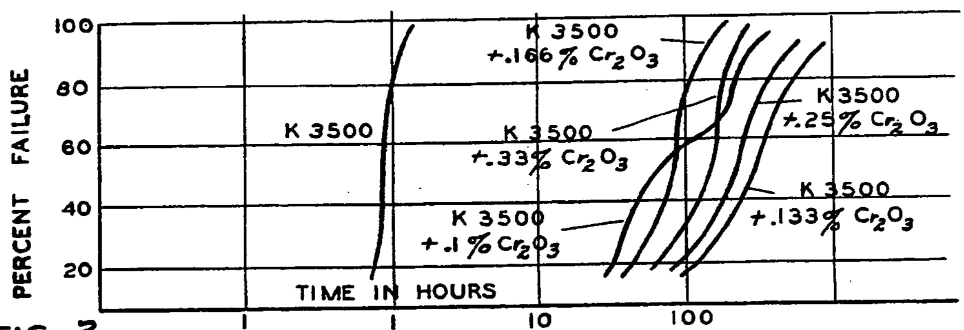

FIG. 2

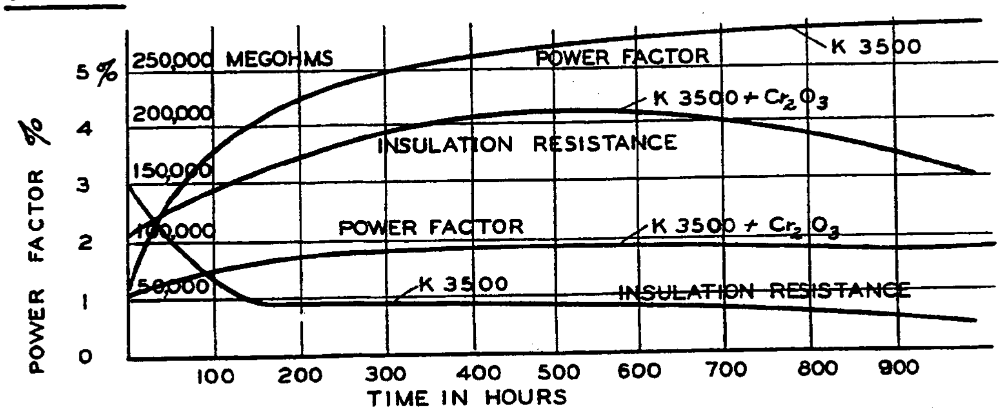

FIG. 3